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(54) Process for laminating thermoplastic resin reinforced with fiber glass

(57) A method of preparing a fiber glass reinforced resin sheet comprising continuously feeding one or more fiber glass mat(s) 102, 103 to a heating zone 120, introducing resin e.g. in the form of sheets 100, 101 into the zone with the mat(s), applying pressure to the mat(s) and resin e.g. by platens 121, 122 at a temperature sufficient to melt the resin and thoroughly wet the mat(s), cooling the mat(s) in a cooling zone 130 to solidify the resin into a resin-mat sheet while maintaining pressure on the resin and mat(s) during cooling e.g. by platens 131, 132 at least equal to the pressure applied to the resin and mat(s) in the heating zone, and removing from the cooling zone a solid sheet of glass mat reinforced resin. In an alternative procedure, pressure is applied by passing the assembly under tension around pressing rollers.

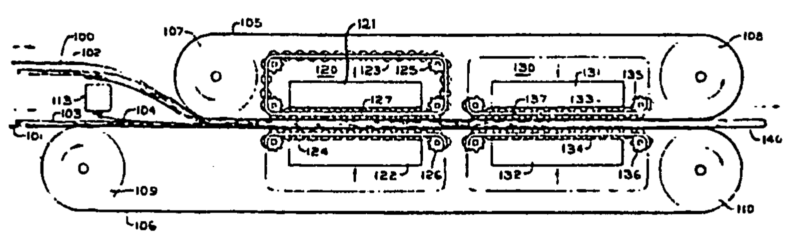

Fig.1

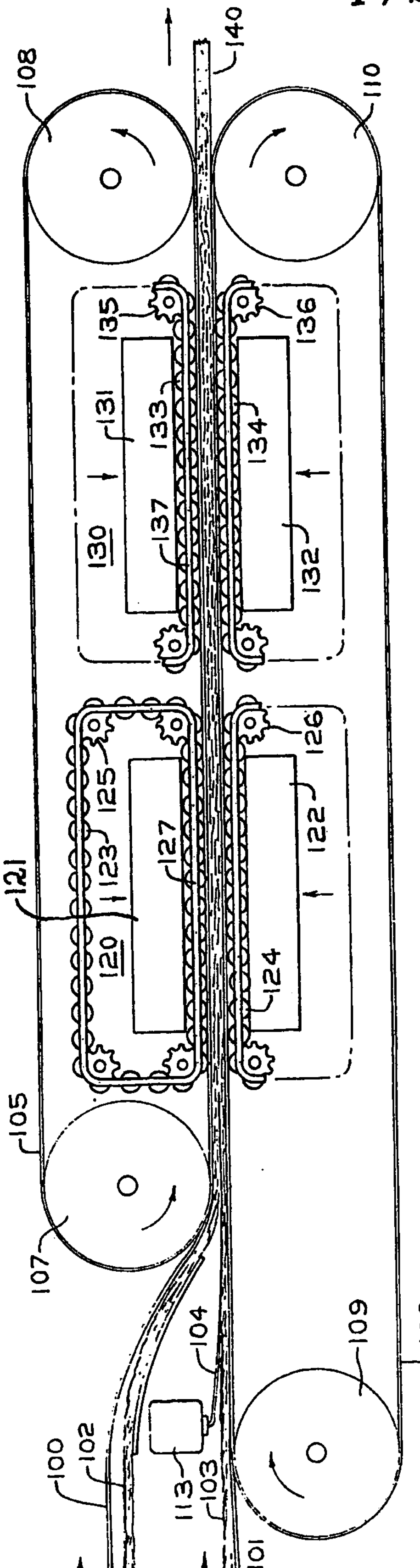

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FIG. 1

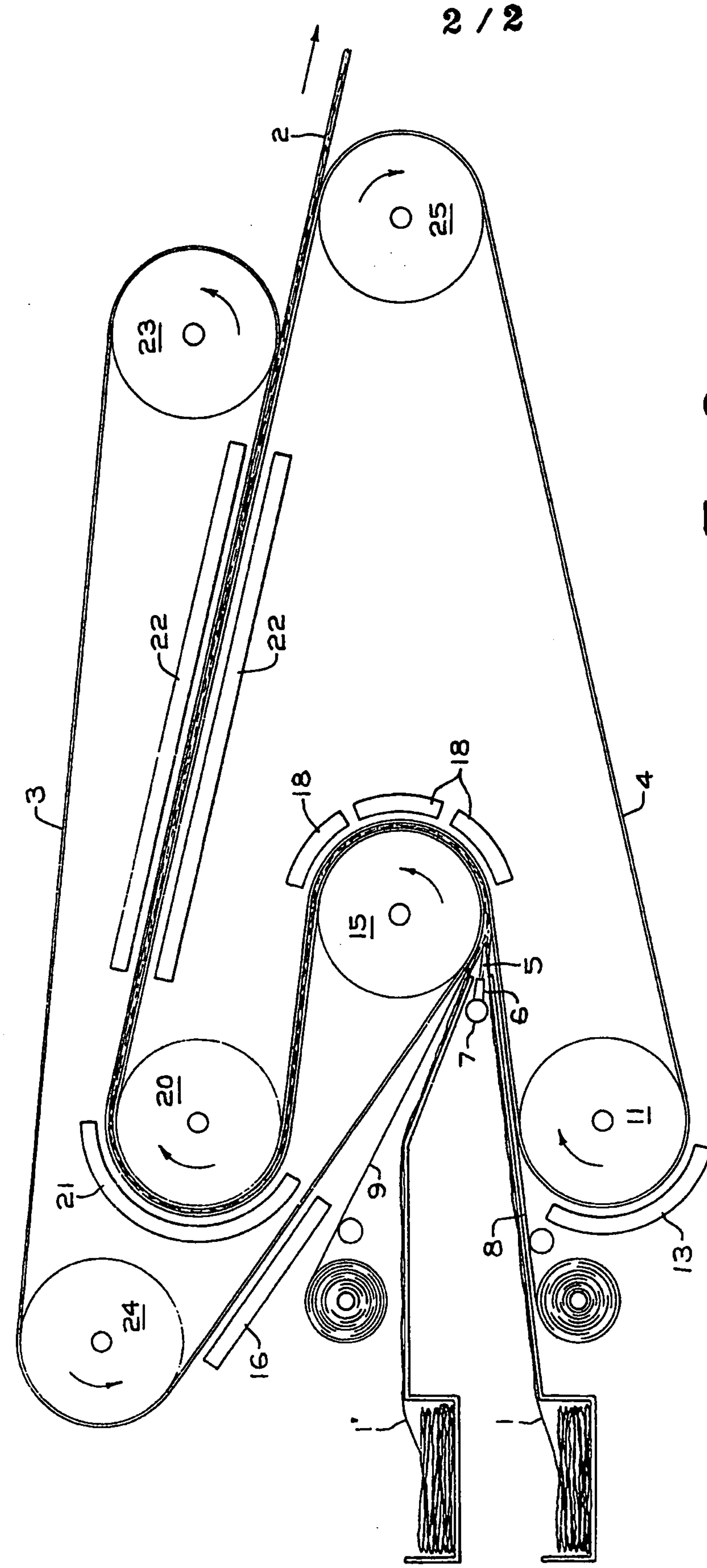

FIG.2

SPECIFICATION

Process for laminating thermoplastic resin reinforced with fiber glass

Fiberglass reinforced thermoplastic sheets capable of being stamped under heat and pressure into a variety of shapes for automotive use have been described in the literature. Typical of methods heretofore employed to produce such products are those described in U.S. Patents 3,664,909; 3,684,645; 3,713,962 and 3,850,723. The glass strands which are used to prepare the mats which are placed in the product are usually treated before mat formation with an appropriate sizing system. One such system is described in U.S. Patent 3,849,148. The mat used in the thermoplastic sheet products produced is typically needled and this is described in U.S. Patents 3,883,333 and 3,664,909.

The laminates produced by the prior art processes and the instant invention may be processed in a stamping operation using the procedures described in U.S. Patents 3,621,092 and 3,626,053.

In the prior art processes above described, layers of needled mat and thermoplastic resin, polypropylene being typical, are laminated in a platen press to produce the sheet product. In another process depicted in Figure 2 of the attached drawings, the lamination of resins and mat takes place in a continuous laminator.

In the process employing the platen press acceptable product is produced, but the manufacturing process itself is slow and costly since the mats and thermoplastic sheets used to make the laminates are laid up by hand and the process is by its nature a batch operation. In the continuous process depicted in Figure 2, inadequate control of the pressure exerted on the laminate in the cooling section frequently results in the production of laminates having nonuniform void content.

In accordance with the instant invention a process for producing a laminated fiber glass reinforced thermoplastic resin continuously is provided which overcomes many of the shortcomings of the prior art. The process of the invention involves passing a fiber glass mat and the thermoplastic resin into a laminating zone which has two distinct temperature regimes. In the first section of the lamination zone, heat and pressure are applied to the thermoplastic resin and glass mat to ensure that the resin is maintained in the molten state during its passage through the zone. The mat and molten resin during their passage through this zone are given sufficient residence time to permit the molten resin to flow through the glass mat and thoroughly impregnate it. The mat and molten resin sheet are then passed into a cooling zone which is maintained under pressure to solidify the resin throughout the mat and provide at the exit end of the cooling section of the laminating process a continuous sheet of fiber glass reinforced thermoplastic having a controlled void content and which is capable of being stamped into a finished part utilizing the stamping procedures of the prior art hereinabove described.

Various thermoplastic resins may be employed to produce laminates in accordance with the instant invention and typical resins suited for this use are homopolymers and copolymers of resins such as: (1) vinyl resins formed by the polymerization of vinyl halides or by the copolymerization of vinyl halides with unsaturated polymerizable compounds, e.g., vinyl esters, alpha, beta-unsaturated acids, alpha, beta-unsaturated esters, alpha, beta-unsaturated ketones, alpha, beta-unsaturated aldehydes and unsaturated hydrocarbons such as butadienes and styrenes; (2) poly-alpha-olefins such as polyethylene, polypropylene, polybutylene, polyisoprene and the like, including copolymers of poly-alpha-olefins; (3) phenoxy resins; (4) polyamides such as polyhexamethylene adipamide; (5) polysulfones; (6) polycarbonates; (7) polyacetals; (8) polyethylene oxide; (9) polystyrene, including copolymers of styrene with monomeric compounds such as acrylonitrile and butadiene; (10) acrylic resins as exemplified by the polymers of methyl acrylate, acrylamide, methylol acrylamide, acrylonitrile and copolymers of these with styrene, vinyl pyridines, etc.; (11) neoprene; (12) polyphenylene oxide resins; (13) polymers such as polybutylene terephthalate and polyethylene terephthalate; and (14) cellulose esters including the nitrate, acetate, propionate, etc. This list is not meant to be limiting or exhaustive but merely to illustrate the wide range of polymeric materials which may be employed in the present invention.

The fiber glass mat used in the preparation of the laminates may be made conveniently by the methods described in U.S. Patent 3,883,333, assigned to the assignee of this invention, and which is incorporated herein by reference. In the method described in this patent the mat is formed by laying down continuous strand on a conveyor surface, typically an intermeshing chain, to the desired depth. The strands are usually placed on the chain by traversing the attenuators that project the strand to the conveyor surface across the width of the surface in a direction transverse of the movement of the conveyor. The mat formed in this manner is then passed through a needling device which is normally a conventional felting loom containing a multiplicity of barbed needles which penetrate the mat causing the continuous strands to become tangled in each other thereby providing dimensional stability to the mat while at the same time breaking them into random lengths. The needling operation provides a significant amount of short glass fibers in the finished mat due to the action of the barbed needles penetrating the depth of the mat and, in doing so breaking a significant number of the continuous strands into short lengths of staple fibers. "Short fibers" as used herein means strands or fibers of 1 inch or less in length. The amount of short fibers produced by the needling operation will vary depending upon the speed of the needling, the number and types of needles used. In general, the short fibers present in the mat range between 10 to 25 percent, preferably between 15 and 20 percent by weight of the mat. The remainder of the mat is composed of strands and fibers in lengths in excess of 1 inch, generally 1-1/2 to 5 inches or longer. As

also shown in the above patent, the speed of the needler and the mat forming surface is coordinated to provide a uniform mat density being recovered from the exit of the needler. The needles employed may contain barbs in either a down or an up position so that upon penetrating the upper mat surface they push fibers from that surface to the interior of the mat or they pull fibers from the under surface of the mat up to the interior, respectively. In some instances needles barbed in both a down and up direction are used to provide for the penetration of strands to the interior from both the upper and the lower surface in a single down and up stroke of the mounting carrying the needles. If desired, the process of the instant invention can also be practiced with chopped strand mats used as the glass source. A typical mat of this type is described in U.S. Patent 2,790,741.

In the practice of the invention the thermoplastic resin may be fed to the laminating process in any of several forms. In some instances the resin is fed to the laminating zone in preformed sheet form of desired thickness and the number of sheets used will depend on the desired thickness of the final product and the mat or mats used. It is also within the purview of the invention to feed the thermoplastic resin to the laminating process as a premelted extrudate from a high temperature, high pressure extrusion line. In this type of system the extrudate is fed between the laminating surfaces in a sheet form, typically from an extrusion die which is maintained at temperature and pressure sufficient to maintain the resin in a flowable state as it is fed to the laminating zone. In a typical operation both molten extrudate is fed to the laminating zone as well as sheet forms of the thermoplastic resin being employed as will be more fully explained hereinafter.

It is also within the purview of this invention to add to the laminates produced by this invention compatible materials which do not affect the basic and novel characteristics of the product. Among such materials are colouring agents, including dyes and pigments, fillers and similar additives. Additives such as antioxidants, bactericides antistatic agents, stabilizers and antimarine fouling agents, may also be added. Generally the quantity of additives if used, are below about 30 percent by weight of the product, typically 10 to 20 percent.

In the practice of the instant invention the laminating process is conducted under various pressure and temperature conditions. Thus, the initial stage of the operation involves contacting the reinforcing fiber glass mat with molten resin to ensure adequate penetration of the mat structure by the resin system being employed to produce the final sheet product. Pressures are exerted in the hot stage portion of the laminating system and may vary from 5 to 120 pounds per square inch, preferably in the range of 20 to 60 pounds per square inch and more preferably from 20 to 30 pounds per square inch. The hot stage of laminating process is typically regulated in a temperature range of 350°F. to 550°F. (117°C. to 288°C.); this temperature being somewhat dependent upon the melt temperatures of the resins employed. For example, with a polypropylene resin system, the temperatures in the hot stage of the laminating typically range between 400°F. to 450°F. (204°C. to 232°C.). In the cold stage of the process, pressures are applied generally at the same magnitude or greater than those used in the hot stage and in general are within the ranges set forth above for the hot stage.

Attention is now directed to the drawing for a further explanation of the invention and its advantages over the prior art.

In the drawings:

Figure 1 is a diagrammatic illustration of a laminating machine suitable for use in producing fiber glass reinforced thermoplastic sheets in accordance with the instant invention.

Figure 2 is a diagrammatic illustration of a continuous laminating process currently in use for producing fiber glass reinforced thermoplastic resin sheets suitable for stamping, and

As shown in Figure 2, a double belt laminating machine is employed to produce a continuous sheet 2 which is composed of a resin and fiber glass mat. In the process depicted fiber glass mats 1 and 1′ are fed between two laminating belts 3 and 4. Molten resin 5 is fed between the mats 1 and 1′ from an adjustable slot 6 located along the length of an extrusion die 7. Two sheets of resin 8 and 9 are fed to the laminating belts 3 and 4 above and below the mats 1′ and 1, respectively.

Belt 4 as it passes round roller 11 is preheated by a heater 13 prior to its engagement with the heating, press roll 15. Similarly, belt 3 is preheated by heater 16 prior to its engagement with press roll 15. The heating, press roll is equipped with heaters 18. Pressure is applied to the laminate 2 by applying tension to the belts 3 and 4. Tension applied to belts 3 and 4 results in the application of radial forces on the resin mat composite. The radial forces and the resulting pressures assist in saturating the mats 1 and 1′ with resin and render sheets 8 and 9 molten when coupled with the heat applied as the tension is applied. Roll 24 applies tension to belt 3 and roll 25 applies tension to belt 4. The material as a compact sheet of resin and fiber glass resulting from the passage of the materials through the press roll 15 is then passed to a cooling roll 20 between the belts 3 and 4 and during its passage over this roll is partially cooled, but not completely solidified. The roll 20 is equipped with a cooler 21 to reduce the temperature of the belts and the resin. The sheet after leaving roll 20 inbetween the belts 3 and 4 is then passed through another elongated cooling zone 22 to further reduce the temperature of the belts 3 and 4 to further cool and solidify the mats and resin into sheet 2. Belt 3 is then reflexed over roll 23 for return to the tension roll 24 and belt 4 is returned over roller 25 to the roll 11 with the product 2 being removed at the point where belts 3 and 4 separate.

While the laminating process depicted has been used to produce useful, commercial products, it has certain shortcomings that the instant invention overcomes. The impregnation pressures are applied to mat and resin by the tension exerted on the belts 3 and 4 by the tension rolls 24 and 25, respectively. Experience has shown that, for example, when a

pressure of 30 pounds per square inch has been applied in the heating press roll 15, only about 1/2 to 1 pound per square inch can be maintained in the cooling area of zone 22. This produces in many instances a larger volume of voids in the product due to the tendency of the glass mat to expand as pressure on it is relaxed thus causing expansion of trapped gases while the resin is not fully solidified. The roll system used and the belt curvatures that are required in this unit also result in uneven belt speeds since, for example, on the press roll 15 the belt 4 is on the outside and in the cooling zone it is on the inside. Thus, belts 3 and 4, which travel at equal linear speeds, move relative to each other on the rolls due to the fact that they pass the rolls at differing radii depending upon which roll they are travelling around.

In the embodiment of the process diagrammatically illustrated in Figure 1, resin sheets 100 and 101, fiber glass mats 102 and 103 and molten resin 104 are fed between belts 105 and 106 of a continuous laminating machine. The belts 105 and 106 are continuous belts which are driven around rolls 107 and 108 and rolls 109 and 110, respectively.

The laminating machine is as shown divided into two distinct sections indicated as 120 and 130. Two sections are shown for convenience only since as will be readily apparent to the skilled artisan, each of these sections may be one or more distinct units. In the illustrated figure, section 120 is the hot lamination zone of the process and it is equipped with an upper platen 121 and lower platen 122 which are movable in a direction perpendicular to the path of travel of belts 105 and 106. These platens 121 and 122 are operated under hydraulic pressure and are capable of exerting forces of 0 to 30 psig to the material being passed through this zone for lamination between belts 105 and 106. With modification the platens can be operated at even higher pressure. Movement of the laminated material through this zone is maintained by a plurality of rollers 123 and 124 located in the upper and lower sections of laminating zone 120, respectively. The rollers 123 and 124 are rods which extend across the width of the belts 105 and 106. They are coupled at their ends by a link chain which in turn rides on the sprockets 125 for rods 123 and sprockets 126 for rods 124. The sprockets 125 and 126 are driven by a suitable motor, not shown. As will be appreciated from the drawing, the laminating pressure applied to the belts 105 and 106 is transmitted to the belts by the rollers 123 and 124 as the platens 121 and 122 contact them. The rollers 123 and 124 move the belts 105 and 106 through the zone 120 while the pressure from the platens 121 and 122 are being applied to the belts 105 and 106 during their passage through this zone.

Zone 120 is also supplied with heat that is transmitted to the sheet material as it passes through zone 120 to maintain it in a molten state and thereby ensure penetration of resin throughout the glass matrix of the laminate being formed.

The laminate passes from zone 120 into zone 130 which is provided with platens 131 and 132 and rollers 133 and 134 in the upper and lower sections thereof, respectively. Similar to zone 120, the rollers 133 and 134 are moved by sprockets 135 and 136 riding on a chain 137 attached to rollers 133 and 134, the sprockets 135 and 136 being driven by a suitable motor assembly (not shown). Platens 132 and 131 apply pressure to the laminate during its passage through zone 130 and zone 130 is supplied with heat transfer fluid in an indirect heat exchange supply systen (not shown) that removes heat from the laminate through rolls 133 and 134 to chill the laminate and solidify the resin throughout. The solid finished product 140 is removed from zone 130 and may then be subjected to slitting, cutting and packaging procedures which form no part of the instant invention.

As will be appreciated by the skilled artisan, the instant process provides considerable flexibility in the physical preparation of laminates of thermoplastic resins reinforced with glass fibers. Thus, pressure may be applied in the hot zone 120 through the use of platens 121 and 122 to any desired degree within the limits of the machine. In general, pressures can be varied from 0 to 30 psig and typically they range from 20 to 30 psig. Similarly in the hot zone 120 heat may be applied in a range of values to ensure adequate flow of resin throughout the glass fiber matrix as the pressure is applied for a given line speed of conveyors or belts 105 and 106. Thus, temperatures of 300°F. to 600°F. (149°C. to 316°C) are typically used in zone 120 to ensure resin temperature in the range of 250°F. to 550°F. (121°C. to 288°C.). It has been found that for a polyolefin a resin temperature range of 400°F. to 450°F. (204°C. to 232°C.) is preferred.

In the operation of zone 130 the application of pressures through platens 131 and 132 as the laminate from zone 120 enters zone 130 can be used to precisely control the void volume of the finished laminate 140; a condition that was not heretofore possible with continuous laminating processes such as shown in Figure 2. Thus, if pressure in zone 130 is maintained at a value greater than that in zone 120 it will result in a low void or almost zero void product. In a typical operation of the system of Figure 2, for example, it has been found that in laminating a polypropylene with glass fiber mats at 30 psig in the hot zone that a pressure of less than 1 psig is realized in the cooling zone 22 and the resulting product has a void content of 8 to 10 percent by volume. Using the process of Figure 1 and applying 30 psig in both the hot zone 120 and the cooling zone 130 a product having 3 to 4 percent voids by volume is typical. Lower void volume content using higher pressures in the cooling zone 130 than used in the heating zone are readily obtained.

Void content may also be controlled to some extent by using molten resin alone without having recourse to laminating systems using sheet products. Thus, by using molten resin 104 alone with mats 102 and 103 and eliminating the overlay sheets 100 and 101, the laminate produced is found to possess considerably less void volume than laminate produced using overlay resin sheets. If surface appearances are not of paramount importance, this provides a useful system for continuous production of low void volume laminates. Coupling this with

careful control of the pressure in the cooling area of the laminating process to maintain it at or greater than the pressure in the heating zone of the process produces laminates having consistently low void volumes.

In general the fiber glass mats employed in the preparation of laminates in accordance with the instant process are needled to provide mat integrity and to supply broken filaments and strands to the mat so that it possesses inherently after needling 10 to 25 percent by weight of the mat of short fibers (i.e. fibers in the range of to 1 inch or less in length) with the balance of the mat being composed of longer strands. The continuous strand mats may be formed by the process of U.S. Patent 3,883,333 from fibers ranging in diameter from a "T" fiber to a "G" or less. The strands of fibers used to prepare the mat are typically in bundles of 50 fibers or less although bundles of fibers with 100 or more filaments may be used.

The continuous strand mat may be prepared directly from a bushing as in U.S. Patent 3,883,333 or it may be formed by drawing strands from previously formed forming packages with a suitable attenuator and laying the strands on a conveyor in a manner similar to that described in U.S. Patent 3,883,333.

In Figure 1 preformed films of thermoplastic 100 and 101 are used with a molten extrudate 104 being placed between the glass mats 102 and 103. It is not necessary that the process be conducted in this manner although this method does represent a preferred method of operation. It is contemplated that the process of the instant invention may be conducted by using multiple layers of extrudate, either from separate extruders or using a single, multiple head extruder. In the latter instance the mats or mat is fed in such a manner that extrudate is fed on the outside of the glass mat as well as on the inside. The advantage of using extrudate in lieu of the film layers 100 and 101 is that the extrudate heat of the molten thermoplastic will not require the heat load in the hot zone 120 that is required to melt the films 100 and 101 and thus the machinery is not subjected to the heating loads used when film is employed. It is also contemplated that a single mat may be used in conjunction with a preformed thermoplastic film or with extrudate alone. It is preferred with single mat structures to employ extrudate rather than film as the thermoplastic source. As stated above the use of extrudate where possible is desirable since the total energy input to the system is reduced if it is applied primarily to the resin employed by the extruder rather than through the indirect heat exchange system of the hot zone of the laminating machine.

While the invention has been described with reference to certain specific embodiments, it is not intended to be limited thereby except insofar as appears in the accompanying claims.

CLAIMS

1. A method of preparing a fiber glass reinforced resin sheet comprising continuously feeding a fiber glass mat to a heating zone, introducing resin in the zone with the mat, applying pressure to the mat and resin at temperature sufficient to maintain the resin molten and thoroughly wet the mat with resin, subjecting the mat to cooling in a cooling zone at a temperature sufficient to solidify the resin into a resin-mat sheet while maintaining pressure on the resin and mat during cooling at least equal to the pressure applied to the resin and mat in the heating zone, and removing from the cooling zone a solid sheet of glass mat reinforced resin.

2. A method as claimed in claim 1 wherein the pressure on the resin and mat in the cooling zone is maintained at a value higher than the pressure on the resin and mat in the heating zone.

3. A method as claimed in claim 1 or 2 wherein the resin is thermoplastic.

4. A method as claimed in claim 1, 2 or 3 wherein the resin introduced into the heating zone is molten.

5. A method as claimed in claim 4 wherein two glass mats are fed into the heating zone and wherein the molten resin is fed between the mats.

6. A method as claimed in claim 5 wherein thermoplastic film is fed into the heating zone onto the outside of each mat, the pressure and temperature being such as to cause the film to become molten.

7. A method as claimed in any of claims 1 to 6 wherein the pressure in the heating zone and the cooling zone are each from 20 to 60 psig.

8. A method as claimed in claim 7 wherein the pressure in the heating zone and the cooling zone are each from 20 to 30 psig.

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